

Group Contribution Method with SAFT EOS Applied to Vapor Liquid Equilibria of Various Hydrocarbon Series

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Abstract

A new group contribution method is proposed using the SAFT (Statistical Associating Fluid Theory) equation of state (EOS), in order to describe the thermodynamic properties of hydrocarbon series. The method is developed for vapor-liquid equilibrium (VLE) calculations for a large number of hydrocarbons, with the use of several group parameters. SAFT models are chosen for the physical meaning of their parameters. These can be related to the molecular structure. Two versions of the SAFT EOS are used in this work: The original SAFT equation of state, proposed by Chapman, *et al.* [*Ind. Eng. Chem. Res.*, 29 (1990) 1709] and SAFT-VR (SAFT Variable Range) equation of state, proposed by Gil-Villegas, *et al.* [*J. Chem. Phys.*, 106 (1997) 4168]. The present group contribution method consists in calculating the equation of state parameters (dispersion energy ϵ , segment diameter σ , chain length m and square-well range parameter l for SAFT-VR) using group contribution rules. In this paper, we have treated pure compounds of five hydrocarbon families: *n*-alkanes, *alkyl*-benzenes, *alkyl*-cyclohexanes, α -olefins and *l*-alkanols. The results obtained are compared with those of the usual approach (fitting the molecular parameters of each compound on its own properties) and seem to be nearly equivalent. The results of the present method are comparable with those of other predictive approaches.

Keywords: equation of state, group contribution, SAFT, vapor liquid equilibria, hydrocarbons, *n*-alkanes, *alkyl*-benzenes, *alkyl*-cyclohexanes, α -olefins, *l*-alcohols.

Introduction

The design of many chemical processes at an industrial scale requires information about the involved chemicals, such as thermophysical and phase equilibria properties. Since experimental measurements are long and costly, the amount of experimental work can be reduced if efficient thermodynamic models are used to calculate the properties at different conditions of pressure and temperature. As systems of interest become more and more complex, models embedding predictive features are more needed since few or even no experimental data are available for some compounds, especially heavy and/or branched molecules.

In the last decades, some fruitful attempts to develop such predictive thermodynamic models were based on the group contribution (GC) concept integrated into an equation of state (EOS). These methods generally assume that a given molecule may be divided into chemical functional groups. Properties and/or equation parameters of the corresponding chemicals are then calculated through formulae accounting for weighted contributions of the different groups present in the molecules.

As it appears from a recent review [1], most of these methods are designed for estimation of pure compounds properties such as critical temperature, pressure, volume and acentric factor that may be further used, for instance, in a cubic equation of state. Some methods provide estimations of these constants within a few percent or even less, if compared to experimental

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values. But even a small error on these constants may lead to a significant effect on the phase equilibrium calculations.

Apart from such procedures, there are mainly two other ways to apply a group contribution to an EOS.

The first way consists in using an activity coefficient model with a built-in group contribution method (see ASOG [2], UNIFAC [3] and extended versions [4]) for calculation of mixture parameters of an EOS through appropriate mixing rules, i.e. the well known G^E mixing rules (for example MHV2 [5,6] and those of Wong and Sandler [7]). In this class of models, falls PSRK (Predictive Soave-Redlich-Kwong) of Gmehling and coworkers [8-13], one of the most widely used and representative equation of this kind. Although good predictions for mixtures are provided by these methods, it is nevertheless necessary to have a good evaluation of the pure compounds parameters. For this reason, such methods cannot be employed alone when the pure parameters of one compound are unknown.

A second way of applying a GC concept, but less widely tested consists in evaluating the EOS parameters using a built-in group contribution rule. Only a few attempts were made in this direction in the last decades. Among the first attempts, one may find GC-EOS of Skjold-Jorgensen [14], later modified by Gros *et al.* [15] by addition of a term for association. In a similar manner, Pulis *et al.* [16] used the Chain Of Rotators (COR) EOS of Chien *et al.* [17] to derive their CORGC equation of state. Most of other similar works are based on lattice fluid theory equations of state and are mainly used for polymer systems. The most extensive work of this type is due to Danner and collaborators [18-22] who have based their GCLF EOS on the equation introduced by Panayiotou and Vera [23,24] and have applied it to a number of systems including polymer solutions until very recently [20-22]. Other Group contribution equations based on the lattice fluid theory include the works of Yoo and Lee [25], Haruki *et al.* [26], Mattedi *et al.* [27] and Rigal [28]. The latter proposed 3 different GC methods based on the Sanchez Lacombe EOS [29]. Thus, the group contribution concept was applied to equations derived either from lattice theory or based on Prigogine theory for chain molecules. A lattice theory appears well adapted for a GC concept.

Although such models have proven their efficiency for representing polymer systems, and other fluid state systems, it originates from a theory for solids. A theory for liquids may be more appropriate for our purposes. An attempt based on the PHSC (Perturbed Hard Sphere-Chain) theory has been proposed by Elvassore *et al.* [30].

In the Prigogine theory, the size parameter c stands for a number of degrees of freedom but not rigorously for a number of chemical groups, even if it has been sometimes correlated to a size parameter of the molecule.

For these reasons, we focused our attention on SAFT EOS. This equation seems adapted for developing a GC method, since it is based on a fluid theory and is an explicit chain model. Here, molecules are indeed divided into several spherical segments with their own parameters, suggesting that a GC concept is easily applicable. But, as far as we know, apart from rules to calculate SAFT parameters for co-polymers [31-34] there is no general group contribution EOS based on a SAFT model.

The aim of this article is to propose a GC method for SAFT EOS. As a first step, we investigated pure compounds with two versions of the SAFT model.

In the subsequent sections, a short presentation of the two SAFT versions is given, then the proposed group contribution scheme is described as well as the determination of the group parameters. The last section is devoted to results and discussion with emphasis on the quality of predicted results i.e. for compounds not present in the regressed database.

SAFT equations of state

SAFT is not a single equation of state, it is rather a class of equations based on the same general ideas. Here, molecules are considered as chains of identical spherical segments that may form associating links with other molecules. They are generally expressed in the form of residual Helmholtz free energy terms accounting for different effects.

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \quad (1)$$

Notice that here, a stands for the reduced molar free energy i.e. $a = \frac{A}{nRT}$

The first term accounts for the attractive-repulsive contribution of a single segment. It is written as:

$$a^{seg} = m a_0^{seg} \quad (2)$$

where m is the chain length parameter i.e. the number of segments constituting the chain and a_0^{seg} is the reduced residual Helmholtz free energy for one mole of spherical segments. As pointed out by Müller and Gubbins [35], SAFT does not specify the expression for this term, each version will have its own expression depending on the choice of the potential and the approximations used. A brief description of this term for the two equations used in this work is given below.

The chain term is used to model non-spherical molecules as chains of tangentially bonded spheres. This term a^{chain} is derived from the association term in the limit of infinitely strong association between two spheres of diameter d . The expression determined by Chapman [36] uses the cavity function y evaluated at the contact value d .

$$a^{chain} = -(m-1) \ln y(d) \quad (3)$$

Here again, different versions of SAFT use different expressions depending on the assumptions made. See below for the two models selected in this study.

Finally, the association term (a^{assoc}) is based on the results of Wertheim [37-41]. This term is written as a sum over all association sites of the molecule.

$$a^{assoc} = \sum_{A=1}^S \left[\ln X^A - \frac{X^A}{2} \right] + \frac{1}{2} S \quad (4)$$

where S is the number of sites on the molecule and X^A is the mole fraction of the molecules that are *not* bonded at site A . This quantity is then related to the association parameters through the following set of non linear equations:

$$X^A = \left[1 + N_{Av} \sum_{B=1}^S r X^B \Delta^{AB} \right]^{-1} \quad (5)$$

Here, the function Δ^{AB} characterizes the association strength. The approximation given by Jackson *et al.* [42] uses the contact value of the segment radial distribution function $g^{seg}(d)$, the association potential for the site-site A-B interaction and introduces the bonding volume parameter k^{AB} to account for the associating range.

$$\Delta^{AB} = k^{AB} g^{seg}(d) \left[\exp \frac{e^{AB}}{kT} - 1 \right] \quad (6)$$

Hence, the association term depends on two association parameters e^{AB} and k^{AB} for each associative A-B interaction considered.

The set of equations (5) depends on the system considered and can be solved numerically for the general case. In this work, we only consider 1-alkanols with an association model denoted

as 3B by Huang and Radosz [43,44]. This association model considers three association sites A,B,C of which two are identical (A=B) and only one association strength is considered nonzero: $\Delta = \Delta^{AC} = \Delta^{BC}$. In this case, there is an analytical solution for the unknown molar fractions of equations (5):

$$\begin{cases} X^A = X^B = \frac{-(1 - N_{Av} r \Delta) + \sqrt{(1 + 4 N_{Av} r \Delta)^2 + 4 N_{Av} r \Delta}}{4 N_{Av} r \Delta} \\ X^C = 2 X^A - 1 \end{cases} \quad (7)$$

The association term in the two versions of SAFT used in this work will only differ in the approximation of the radial distribution function $g(d)$.

Versions of SAFT used in this work

Two different versions of SAFT were used in this work:

The first one is the original SAFT equation, due to Chapman, *et al.* [45] and is denoted in this article by SAFT-0.

This version uses for segment-segment interaction a Lennard-Jones potential treated by a perturbation method (Barker Henderson [46]). The reference is a hard sphere system with a temperature dependent sphere diameter. Unlike in the original work of Chapman *et al.* [45], and since we do not want a hard sphere diameter dependent on chain length m , we use the original equation fitted by Cotterman *et al.* [47].

$$\frac{d}{s} = \frac{1 + 0,2977 \frac{T_R}{T_R + 0,0010477 T_R^2}}{1 + 0,33163 \frac{T_R}{T_R + 0,0010477 T_R^2}} \quad (8)$$

Here, the expression of Carnahan and Starling [48] is used for the hard sphere reference part and an expression due to Cotterman *et al.* [47] is used for the perturbation part.

In this version, the chain term reduces to:

$$a^{chain} = -(m-1) \ln g^{hs}(d) \quad (9)$$

where g^{hs} is the hard sphere radial distribution function for which the expression of Carnahan and Starling is used.

The same hard sphere approximation is used for g^{hs} in the association term given above.

The second version used in this document is called SAFT-VR (SAFT Variable Range), and was developed by Gil-Villegas, *et al.* [49]. The main difference with the SAFT-0 EOS is the interaction potential model. Here, a square-well potential with a variable width is used. Therefore, there is an additional parameter λ accounting for the potential width.

The segment-segment interaction is treated by the perturbation theory of Barker Henderson [50] i.e an expansion of the free energy in the variable $1/kT$ at the second order. The zeroth order represents the reference hard sphere system for which the Carnahan and Starling expression is used. Notice that here the hard sphere diameter $d=s$ is not temperature dependent.

The chain term reduces here to:

$$a^{chain} = -(m-1) \left(\frac{e}{kT} + \ln g^{seg}(s) \right) \quad (10)$$

Another difference with the SAFT-0 equation is that the radial distribution function for segments g^{seg} is approximated here by an expansion at the first order (for the square-well potential) while only the hard sphere approximation is used in SAFT-0.

The association term also uses this first order approximation for g^{seg} . This is the only difference in the association term with the SAFT-0 version.

The corresponding mathematical expressions for both used equations of state are described in several references. For a detailed description, the reader is referred to the work of Chapman, *et al.* [45] for the SAFT-0 EOS, and Gil-Villegas, *et al.* [49] for the SAFT-VR EOS.

For our purpose, what is important is to clearly identify the equation parameters and their physical meaning as summarized in Table 1. Note that only one set of association parameters will be used since only the alcohol function will be considered here.

Table 1: Summary of the parameters (and their physical meaning) required for the two equations considered in this work

| | SAFT-0 parameters | SAFT-VR Parameter | Unit |
|------------------------------|----------------------|----------------------|------|
| Energy parameter | ϵ / k | ϵ / k | K |
| Segment diameter | σ | σ | Å |
| Chain length parameter | M | m | - |
| SAFT-VR range parameter | | l | - |
| Association energy | ϵ^{AB} / k | ϵ^{AB} / k | K |
| Association volume parameter | k^{AB} | k^{AB} | - |

Parameter estimation

It is important to keep in mind that given one molecule, SAFT EOS assumes all the segments of a molecule to be identical. Strictly speaking, this hypothesis should restrict the applicability of the model to uniform molecules in terms of molecular structure i.e. molecules made of strictly identical chemical group. Of course, numerous molecules do not follow this condition, and rigorously the applicability of the model should be very restricted. But the problem may be overcome, as shown by the good results provided in several earlier works [43,44,51,52,53] for a wide variety of chemical compounds.

Most authors determine the EOS parameters by fitting on the pure compounds vapor pressure and liquid molar volume data. This approach is designated as the usual approach in the rest of this document.

In an earlier work [51,54], it was assumed that in first approximation the segment parameters ϵ and σ can be taken identical in a series of chemical compounds. Only the parameter m varied with the chain length. This is a reasonable hypothesis if the chemical groups of the molecules considered are rather similar. Reasonably good representations of VLE data (n -alkanes, some branched alkanes, other hydrocarbons and 1-alkohols) were so obtained. However, discrepancies observed suggest that differences between chemical groups should be taken into account. An other approach taken by several authors [43,44,52,53] is an attempt to do it empirically by establishing, for instance, correlations between the parameters of the model with the total number of carbon n_C or molar weight. Such correlations are based on parameter values obtained by adjustment on individual data for each compound.

In the case of n -alkanes, one obtains the plots of figures 1a and 1b. A global trend of σ and ϵ/k with n_C is indeed observed, but the dispersion is large also. The correlation between the two quantities may be thus doubtful and may even lead to large errors when extrapolating as shown earlier [51,54].

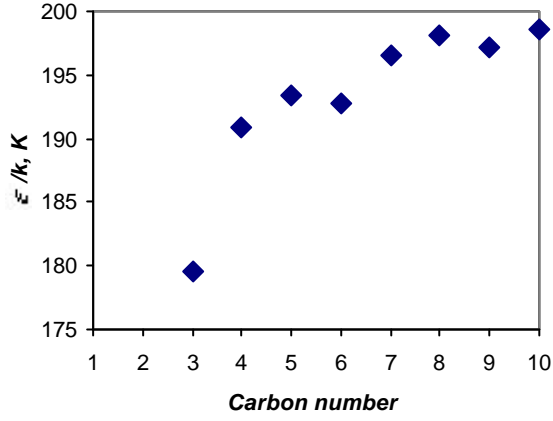


Figure 1a: SAFT-0 EOS dispersion energy fitted on separate pure *n*-alkanes

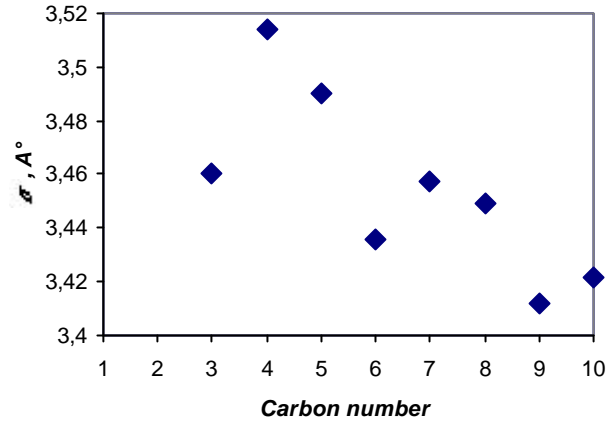


Figure 1b: SAFT-0 EOS segment diameter fitted on separate pure *n*-

For our purposes, we chose to follow another way for parameter estimation and focused then on group contribution methods. Here, the 3 segment parameters are calculated through appropriate averages inspired by the Lorentz-Berthelot combining rules. In these rules, energy parameters are averaged geometrically whereas size parameters are averaged arithmetically. This leads us to:

$$\mathbf{e}_{molecule} = \sum_{i=1}^{n_{groups}} n_i \sqrt{\left(\prod_{i=1}^{n_{groups}} \mathbf{e}_i^{n_i} \right)} \quad (11)$$

$$\mathbf{s}_{molecule} = \sum_{i=1}^{n_{groups}} n_i \mathbf{s}_i / \sum_{i=1}^{n_{groups}} n_i \quad (12)$$

$$\mathbf{l}_{molecule} = \sum_{i=1}^{n_{groups}} n_i \mathbf{l}_i / \sum_{i=1}^{n_{groups}} n_i \quad (13)$$

Of course equation (13) stand only for SAFT-VR.

In these equations, it is important to notice that subscript *i* refers to a specific chemical group. Also, *n_i* is the number of chemical groups of type *i*, and *n_{groups}* is the total number of chemical group in the molecule. The parameters *e_i*, *s_i*, and *l_i*, are related to group *i*.

As noticed several times in earlier works, the chain parameter *m* fits neither the carbon number nor generally an integer value. However in several earlier works [43,44,51,54], it was successfully correlated through a linear correlation to a carbon number *n_C*. In the same spirit, the chain parameter *m*, is assumed to be computed linearly with the number of considered chemical groups.

$$m_{molecule} = \sum_{i=1}^{n_{groups}} n_i R_i \quad (14)$$

where *R_i* is the contribution of the group *i* to the chain length of the molecule model.

Each group is thus characterized by 3 or 4 parameters (depending on the version of the EOS). In order to determine those and test the GC method, several families of chemical compounds were investigated. They are the following:

- *n*-alkanes
- *a*-olefines
- *alkyl*-benzenes
- *alkyl*-cyclohexanes
- *l*-alkanols

This approach (see table 2) introduces explicitly the following groups: (CH₂), (CH₃) and (OH). The sequence CH₂=CH- in α -olefins family may be regarded as one chemical group in the sense that the individual groups CH₂= and =CH- are always together. As a consequence also, it is not possible to uncorrelate the individual effect of CH₂= and =CH- groups on thermodynamic properties of the compound. For this reason, it was decided to consider CH₂= and =CH- both together. Since the group CH₂=CH- is not spherical, it is expected not to be well represented by only one segment of SAFT EOS. Therefore we assumed here it may be split into two identical new groups denoted (C=) _{α -olefins}. In the same spirit, we introduced new groups denoted (C=)_{Bz} and (C-)_{Ch} to model the cyclic part (C₆H₅- and C₆H₁₁-) of *alkyl*-benzenes and *alkyl*-cyclohexanes. Six of these new groups were considered for the representation of the cycle in these molecules.

In table 2, the decomposition into groups of the different chemical families is presented.

Table 2: Decomposition of molecules into groups for the different chemical families

| Molecules | number of groups | | | | | |
|---|------------------|-----------------|---|--------------------|--------------------|----|
| | CH ₂ | CH ₃ | (C=) _{α-olefins} | (C=) _{Bz} | (C-) _{Ch} | OH |
| <i>n</i>-alkanes | | | | | | |
| CH ₃ -(CH ₂) _{nC-2} -CH ₃ | nC-2 | 2 | 0 | 0 | 0 | 0 |
| <i>a</i>-olefines | | | | | | |
| CH ₂ =CH-(CH ₂) _{nC-4} -CH ₃ | nC-4 | 1 | 1 | 0 | 0 | 0 |
| <i>Alkyl</i>-benzenes | | | | | | |
| C ₆ H ₅ -(CH ₂) _{nC-1} -CH ₃ | nC-1 | 1 | 0 | 6 | 0 | 0 |
| <i>Alkyl</i>-cyclohexanes | | | | | | |
| C ₆ H ₁₁ -(CH ₂) _{nC-1} -CH ₃ | nC-1 | 1 | 0 | 0 | 6 | 0 |
| <i>l</i>-alkanols | | | | | | |
| CH ₃ -(CH ₂) _{nC-1} -OH | nC-1 | 1 | 0 | 0 | 0 | 1 |

In order to test as far as possible the transferability of the parameters, the values of the above described group parameters were determined by successive steps in the same spirit as that of Mattedi *et al.* [27]. First, the parameters of (CH₂) and (CH₃) groups were determined by regression of *n*-alkane data from *n*-C₃ to *n*-C₁₀. Their values were subsequently re-used for other molecules with an aliphatic part. Second, the parameters of (C=)_{Bz}, (C-)_{Ch}, (C=) _{α -olefin} and (OH) groups were adjusted respectively on *n*-*alkyl*-benzenes (ethyl to decyl benzenes), *n*-*alkyl*-cyclohexanes (ethyl to decyl cyclohexane), *a*-olefins (butene to decene), and *l*-alkanols (1-ethanol to 1-decanol). For these alkanols, as already explained, the selected association model is 3B as denoted by Huang and Radosz [43]. Note that the associating parameters (e^{AB}/k and k^{AB}) are taken identical for all the *l*-alkanols. This is consistent with the spirit of the GC method and it is reasonable to neglect any effect of the carbon chain on the chemical group -O-H.

The parameters values were adjusted simultaneously on vapor pressures and saturated liquid volumes. The regression function that was used is written as:

$$F_{Reg} = \frac{1}{nP} \sum_1^{nP} \left(\frac{P^{cal} - P^{exp}}{P^{exp}} \right)^2 + \frac{1}{nv} \sum_1^{nv} \left(\frac{v_{liq}^{cal} - v_{liq}^{exp}}{v_{liq}^{exp}} \right)^2 \quad (15)$$

where n_P and n_v are respectively, the numbers of the experimental vapor pressures and saturated liquid volumes data.

The vapor pressures and the liquid molar volumes data were chosen regularly spaced in the whole temperature range $[0.4T_c, T_c]$. Two databases are used in this work: experimental data for n -alkanes are taken from the 1999 version of the DIPPR [55] (*Design Institute for Physical Property Data*) database. For other compounds, experimental data are provided from the 2002 version of DIPPR [56]. It should be noted that for those compounds, all the experimental data used are accepted by DIPPR (2002) [56], with a maximum deviation of 5% on vapor pressures and 1% on saturated liquid volumes.

The vapor liquid calculation is based on a bubble point determination for each point (*temperature and liquid composition*), by an iterative routine. The solution is obtained when the fugacity coefficients of the two phases are equal. For the minimization of the objective function, a Levenberg-Marquardt algorithm was used.

Table 3: Group contribution parameters for SAFT-0 and SAFT-VR EOS

| Equation | Parameter | Group parameters | | | | | |
|----------|----------------|-------------------|-----------------|------------------------|--------------------------|------------------------------|--------------------|
| | | CH ₂ | CH ₃ | (C=) α -olefins | (C-)Bz | (C-)Ch | OH |
| | | <i>n</i> -alkanes | | <i>a</i> -olefins | <i>n</i> -alkyl-benzenes | <i>n</i> -alkyl-cyclohexanes | <i>l</i> -alkanols |
| SAFT-0 | e/k (K) | 208.1 | 167.9 | 186.6 | 243.5 | 240.0 | 279.9 |
| | s (A°) | 3.415 | 3.510 | 3.412 | 3.450 | 3.687 | 2.873 |
| | R | 0.505 | 0.860 | 0.643 | 0.423 | 0.414 | 0.925 |
| | e^{AB}/k (K) | - | - | - | - | - | 2212.0 |
| | k^{AB} | - | - | - | - | - | 0.0138 |
| | | | | | | | |
| SAFT-VR | e/k (K) | 136.4 | 202.9 | 280.7 | 165.6 | 233.2 | 328.2 |
| | s (A°) | 3.421 | 3.540 | 3.952 | 3.428 | 3.96 | 2.966 |
| | l | 1.900 | 1.468 | 1.466 | 1.875 | 1.704 | 1.551 |
| | R | 0.470 | 0.799 | 0.410 | 0.385 | 0.303 | 0.817 |
| | e^{AB}/k (K) | - | - | - | - | - | 2170.0 |
| | k^{AB} | - | - | - | - | - | 0.0112 |

The obtained values for the group parameters are summarized in table 3. The orders of magnitude appear physically reasonable.

Results

In this section, the results of data correlation are first presented. Then the predictive ability of the method is tested on several heavy compounds not present in the regressed database.

Data correlation

Relative deviations obtained with the group contribution parameters on the vapor pressures and saturated liquid volumes for pure compounds of the regressed database are presented in Table 4.

Table 4: Relative deviations of vapor pressures and saturated liquid volumes of the regression database compounds with the SAFT-0 and SAFT-VR EOS

| Corps | Vapor pressures | | | | Saturated liquid volumes | | | |
|----------------------------|-----------------|-----|--------------------------|---------|--------------------------|-----|--------------------------|---------|
| | T range (K) | Npt | AAD P^{sat} (%) | | T range (K) | Npt | AAD v^{liq} (%) | |
| | | | SAFT-0 | SAFT-VR | | | SAFT-0 | SAFT-VR |
| <i>n</i> -alkanes | | | | | | | | |
| Propane | 151 – 366 | 12 | 1.46 | 2.14 | 151 – 361 | 12 | 1.59 | 2.18 |
| <i>n</i> -butane | 175 – 420 | 13 | 2.24 | 1.62 | 175 – 415 | 13 | 1.38 | 1.70 |
| <i>n</i> -pentane | 188 – 463 | 15 | 2.32 | 1.70 | 188 – 458 | 15 | 1.85 | 1.91 |
| <i>n</i> -hexane | 208 – 503 | 16 | 3.10 | 2.49 | 208 – 498 | 16 | 2.26 | 2.11 |
| <i>n</i> -heptane | 218 – 538 | 17 | 2.68 | 1.13 | 218 – 533 | 17 | 2.57 | 2.34 |
| <i>n</i> -octane | 231 – 561 | 18 | 3.01 | 1.20 | 231 – 556 | 18 | 2.67 | 2.30 |
| <i>n</i> -nonane | 240 – 590 | 19 | 3.09 | 1.28 | 240 – 585 | 19 | 3.00 | 2.63 |
| <i>n</i> -decane | 249 – 614 | 19 | 3.16 | 1.78 | 249 – 609 | 19 | 3.04 | 2.71 |
| <i>Alkyl</i> -Benzenes | | | | | | | | |
| Ethyl-Bz | 283 – 617 | 30 | 8.12 | 4.93 | 243 – 603 | 24 | 5.63 | 3.80 |
| <i>n</i> -propyl-Bz | 266 – 433 | 13 | 3.48 | 3.08 | 253 – 373 | 13 | 0.92 | 1.34 |
| <i>n</i> -butyl-Bz | 269 – 523 | 26 | 3.44 | 2.11 | 263 – 423 | 17 | 1.19 | 1.82 |
| <i>n</i> -pentyl-Bz | 353 – 510 | 19 | 2.23 | 2.09 | 263 – 453 | 20 | 1.65 | 2.32 |
| <i>n</i> -hexyl-Bz | 329 – 531 | 22 | 2.48 | 2.61 | 273 – 453 | 19 | 1.58 | 2.20 |
| <i>n</i> -heptyl-Bz | 321 – 552 | 20 | 2.03 | 2.11 | 283 – 453 | 18 | 1.52 | 2.02 |
| <i>n</i> -octyl-Bz | 316 – 571 | 27 | 2.50 | 2.31 | 283 – 453 | 18 | 1.76 | 2.19 |
| <i>n</i> -nonyl-Bz | 332 – 589 | 27 | 2.94 | 3.34 | 293 – 453 | 17 | 1.85 | 2.11 |
| <i>n</i> -decyl-Bz | 371 – 606 | 24 | 4.45 | 4.11 | 293 – 453 | 17 | 2.08 | 2.21 |
| <i>Alkyl</i> -cyclohexanes | | | | | | | | |
| <i>n</i> -ethyl-Ch | 294 – 433 | 15 | 2.11 | 3.03 | 250 – 383 | 14 | 1.71 | 1.15 |
| <i>n</i> -propyl-Ch | 313 – 459 | 15 | 1.70 | 2.62 | 250 – 383 | 13 | 1.03 | 0.97 |
| <i>n</i> -butyle-Ch | 333 – 484 | 21 | 1.13 | 3.12 | 255 – 383 | 24 | 1.08 | 1.04 |
| <i>n</i> -decyl-Ch | 325 – 645 | 33 | 1.74 | 3.55 | 273 – 383 | 12 | 3.12 | 2.19 |
| <i>a</i> -oléfins | | | | | | | | |
| <i>I</i> -butene | 196 – 416 | 19 | 1.94 | 1.85 | 195 – 410 | 19 | 1.99 | 2.96 |
| <i>I</i> -pentene | 218 – 463 | 23 | 2.37 | 1.97 | 267 – 453 | 19 | 1.39 | 2.01 |
| <i>I</i> -hexene | 250 – 504 | 16 | 3.48 | 1.92 | 213 – 339 | 13 | 1.62 | 0.68 |
| <i>I</i> -heptene | 267 – 392 | 13 | 1.93 | 1.00 | 223 – 363 | 14 | 2.19 | 1.08 |
| <i>I</i> -octene | 274 – 421 | 14 | 1.97 | 0.85 | 293 – 393 | 11 | 1.50 | 0.84 |
| <i>I</i> -nonene | 309 – 448 | 13 | 1.72 | 0.95 | 273 – 393 | 13 | 2.24 | 1.19 |
| <i>I</i> -decene | 315 – 593 | 24 | 2.43 | 2.47 | 273 – 393 | 13 | 2.71 | 1.34 |
| <i>I</i> -alkanols | | | | | | | | |
| <i>I</i> -ethanol | 243 – 514 | 14 | 3.50 | 4.93 | 223 – 473 | 13 | 1.49 | 0.81 |
| <i>I</i> -propanol | 273 – 537 | 15 | 3.66 | 4.45 | 153 – 483 | 18 | 0.80 | 1.13 |
| <i>I</i> -butanol | 296 – 563 | 15 | 2.27 | 3.48 | 186 – 490 | 16 | 1.05 | 1.91 |
| <i>I</i> -pentanol | 287 – 573 | 16 | 3.56 | 3.65 | 253 – 490 | 15 | 1.41 | 2.07 |
| <i>I</i> -hexanol | 310 – 603 | 16 | 2.59 | 1.43 | 253 – 413 | 9 | 1.94 | 2.03 |
| <i>I</i> -heptanol | 316 – 603 | 16 | 2.85 | 2.82 | 253 – 413 | 10 | 2.55 | 2.16 |
| <i>I</i> -octanol | 293 – 549 | 12 | 1.93 | 2.54 | 253 – 490 | 13 | 2.39 | 2.80 |
| <i>I</i> -nonanol | 365 – 613 | 14 | 1.64 | 1.64 | 273 – 328 | 6 | 4.00 | 3.70 |
| <i>I</i> -decanol | 336 – 528 | 10 | 0.74 | 1.95 | 283 – 553 | 14 | 2.82 | 3.10 |

$$AAD\ X\ \% = \frac{100}{N_X} \sum_i^{N_X} \frac{|X_i^{\text{cal}} - X_i^{\text{exp}}|}{X_i^{\text{exp}}}$$

From this table, it appears that the accuracy of the method with both versions of SAFT is good (generally within 3 % on vapor pressures and 2 % on saturated liquid volumes). These results are particularly satisfactory since the temperature range of the fitted data is wide. Moreover, these results compare well with those obtained using the usual approach. The latter gives generally deviations of the order of 1-2% on such compounds. Notice that the usual method provides the lowest deviations but requires specific (*i.e non-transferable*) parameters for each compound.

It should be noted that for the families other than *n*-alkanes, the use of aliphatic chain parameters that were transferred from the fit on the *n*-alkanes gives good results. Such a parameter transfer is not always possible with other approaches. For example, the method proposed by Benzaghoul *et al.* [51,54] did not allow the complete transferability of the segment parameters from the *n*-alkanes to the *1*-alkanols [57].

Prediction

VLE calculations of heavier compounds using the group contribution method without adjustment on experimental data is a pertinent test of the predictive character of the approach. The results obtained on several representative compounds are displayed in tables 5 and 6 along with those obtained by other methods for comparison.

The comparison is extensive with the usual approach (direct fit of the experimental data) and the method proposed by Benzaghoul *et al.* since all calculations were performed exactly on the same data. Notice that the method of Benzaghoul *et al.* is used here, with parameters determined for each chemical series.

The comparison with other methods is not very easy since the different authors (i) use different strategies for group parameters regression on more or less wide compounds databases with or without mixtures and for different target systems, (ii) apply their methods to compounds other than those investigated here, (iii) give average deviations for data sets and data ranges different from those used in this study, (iv) do not always give details on the database so true prediction cannot be distinguished from correlation.

At least in the case of the work of Mattedi *et al.* [27] was it possible to give deviations for the vapor pressures on the same temperature ranges as a basis for comparison on a few compounds. The conclusion deduced from the latter comparison should be taken with care, since, not only different experimental data were used by Mattedi *et al.*, but also their group parameters were adjusted on pressures only (vapor pressures and bubble pressures of binary mixtures). Direct comparison with other works is even more problematic. Suffice it to say that the reported deviations for true predictions on similar compounds are generally of the same order of magnitude or higher. See for example Elvassore *et al.* [30] or Rigal [28].

Examination of Tables 5 and 6 shows that the deviations are slightly higher with group contribution than with parameters fitted on the data but still remain satisfactory especially if one reminds that they are pure predictions. Generally, but not always, SAFT-VR group contribution predictions are better than SAFT-0 ones. Anyway, SAFT-VR behaves better than SAFT-0 with this method while it was not the case with the method of Benzaghoul *et al.* Another thing interesting to note is that for *n*-alkanes at least, the deviations remain relatively stable when the chain length increases. This makes us confident that this method may be applied successfully for polymers. As a matter of fact, the GC deviations increase slightly with chain length but so do the deviations of the usual method which represent the best fit to the data with the given equation. This may be due to the fact that, as pointed out elsewhere by us [51] and others [58], because of the low-pressure range, the accuracy of the data decreases for longer chains.

Table 5: deviations of predicted vapor pressures for heavier compounds

| Compound | Temperature range (K) | Npt. | Method | | | | | | Mattedi <i>et al.</i> |
|-------------------------------|-----------------------|------|-----------------------------------|---------|---------------------------------|---------|-------------------------|---------|-----------------------|
| | | | This work (Group Contribution) | | Usual approach (correlation) | | Benzaghou <i>et al.</i> | | |
| | | | SAFT-0 | SAFT-VR | SAFT-0 | SAFT-VR | SAFT-0 | SAFT-VR | |
| <i>n</i> -C ₁₆ | 291 – 721 | 30 | 7.38 | 4.46 | 4.26 | 1.75 | 16.17 | 44.61 | - |
| | 391 – 581 | 20 | 6.83 | 5.02 | - | - | - | - | 2.87 |
| <i>n</i> -C ₂₂ | 317 – 782 | 32 | 16.19 | 6.12 | 4.21 | 3.04 | 20.88 | 75.78 | - |
| | 452 – 572 | 13 | 13.16 | 2.91 | - | - | - | - | 9.16 |
| <i>n</i> -C ₂₄ | 324 – 804 | 33 | 20.09 | 8.13 | 7.56 | 3.24 | 21.76 | 84.46 | - |
| | 453 – 589 | 15 | 13.23 | 5.58 | - | - | - | - | 11.73 |
| <i>n</i> -C ₂₅ | 327 – 804 | 33 | 20.72 | 7.62 | 6.72 | 2.66 | 23.07 | 92.68 | - |
| <i>n</i> -C ₂₈ | 334 – 829 | 34 | 23.04 | 7.06 | 6.44 | 6.14 | 29.50 | 116.99 | - |
| | 484 – 590 | 12 | 20.30 | 3.97 | - | - | - | - | 18.49 |
| <i>n</i> -C ₃₂ | 342 – 852 | 35 | 30.64 | 12.10 | 9.04 | 7.67 | 33.88 | 146.87 | - |
| <i>l</i> -C ₁₂ -OH | 298 – 619 | 26 | 4.86 | 7.67 | 2.32 | 1.55 | 7.52 | 7.22 | - |
| <i>l</i> -C ₁₈ -OH | 365 – 760 | 17 | 11,33 | 4,84 | - | 0.82 | 23.06 | 12.78 | - |
| <i>n</i> -C ₁₈ -Bz | 484 – 834 | 9 | 23,41 | 7,38 | 6.76 | 2.42 | 27.37 | 10.68 | - |
| <i>l</i> -C ₁₈ = | 375 – 703 | 24 | 6,76 | 6,93 | 2.28 | 1.53 | 5.17 | 30.78 | - |

It may be amazing that in some cases, group contribution may give better liquid volume results than the direct fit of data. But if one reminds that both pressures and volumes are used for the fit, there is no contradiction, since the GC pressure deviations are greater and so are the overall deviations.

Table 6: deviations of predicted saturated liquid volumes for heavier compounds

| Compound | Temperature range (K) | Npt. | Method | | | | | |
|-------------------------------|-----------------------|------|-----------------------------------|---------|---------------------------------|---------|-------------------------|---------|
| | | | This work (Group Contribution) | | Usual approach (correlation) | | Benzaghou <i>et al.</i> | |
| | | | SAFT-0 | SAFT-VR | SAFT-0 | SAFT-VR | SAFT-0 | SAFT-VR |
| <i>n</i> -C ₁₆ | 291 – 721 | 30 | 3.93 | 3.97 | 4.46 | 3.15 | 14.10 | 20.23 |
| <i>n</i> -C ₂₂ | 317 – 782 | 32 | 4.39 | 5.10 | 5.16 | 3.45 | 18.53 | 31.59 |
| <i>n</i> -C ₂₄ | 324 – 804 | 33 | 4.15 | 4.82 | 5.06 | 2.82 | 17.98 | 34.34 |
| <i>n</i> -C ₂₅ | 327 – 807 | 33 | 4.28 | 5.25 | 5.13 | 2.66 | 19.56 | 33.04 |
| <i>n</i> -C ₂₈ | 334 – 829 | 34 | 4.53 | 5.66 | 6.02 | 3.90 | 20.71 | 36.45 |
| <i>n</i> -C ₃₂ | 342 – 852 | 35 | 3.73 | 4.89 | 6.72 | 6.92 | 20.31 | 35.08 |
| <i>l</i> -C ₁₂ -OH | 298 – 573 | 20 | 3.07 | 6.92 | 2.94 | 1.66 | 2.82 | 1.49 |
| <i>l</i> -C ₁₈ -OH | 333 – 573 | 13 | 2.67 | 3.02 | - | 0.38 | 2.82 | 1.22 |
| <i>n</i> -C ₁₈ -Bz | 313 – 513 | 7 | 3.16 | 3.31 | 2.84 | 0.38 | 10.24 | 8.34 |
| <i>l</i> -C ₁₈ = | 291 – 393 | 13 | 5.15 | 3.65 | 1.11 | 1.80 | 5.42 | 7.00 |

Notice that the temperature ranges given in tables 5 and 6 correspond when data are available to $[0.4T_c, T_c]$ so as to cover the range from the triple point to the critical point

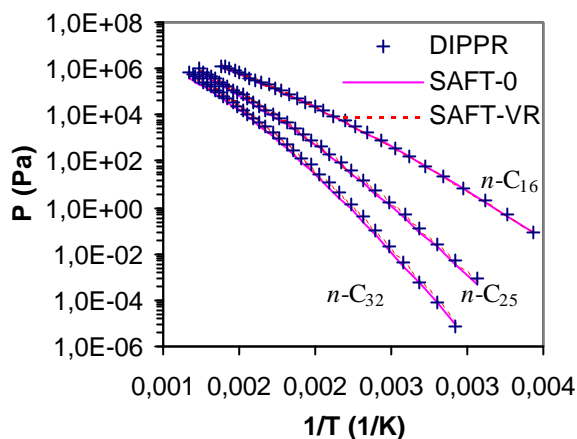


Figure 2a: prediction of the vapor pressures of heavy *n*-alkanes with the group contribution method

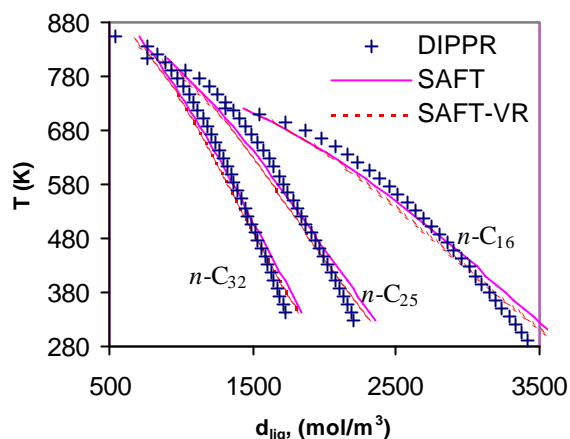


Figure 2b: prediction of the saturated liquid volumes of heavy *n*-alkanes with the group contribution method

As an example of predicted data, figures 2a and 2b shows the vapor-liquid equilibria for the heavier *n*-alkanes (C_{16} , C_{25} , C_{32}). Both equations of state are in reasonable agreement with the DIPPR (1999) [55] vapor pressure and liquid volume data. This trend is also observed on the other chemical series, treated in this work as seen in tables 5 and 6.

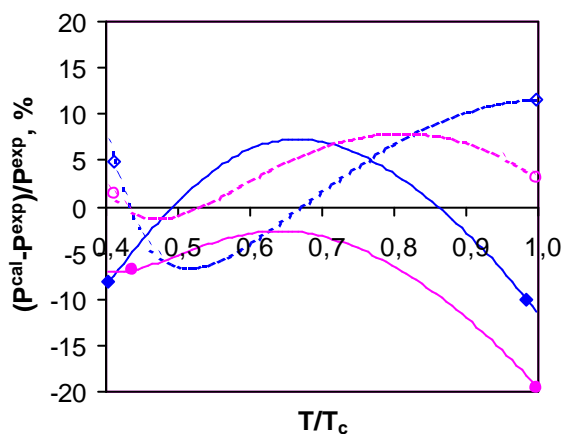


Figure 3a: compared deviations of the predicted vapor pressures of *n*-hexadecane with the group contribution method and the usual method

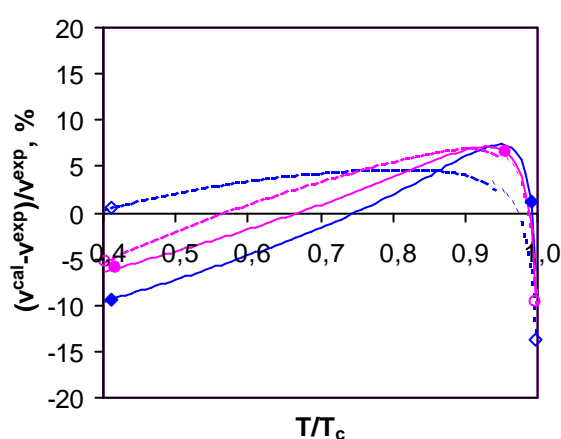


Figure 3a: compared deviations of the predicted saturated liquid volumes of *n*-hexadecane with the group contribution method and the usual method

In figures 3a and 3b, deviations for calculated pressures and liquid volumes of *n*-hexadecane by group contribution and usual approaches are plotted for both SAFT versions. The deviations are distributed differently but they are of the same overall order so that the use of group contribution may be thought of, here, as equivalent to the fit on the experimental data. The deviations for the values calculated with the Benzaghrou *et al.* method were not plotted since they are mostly out of range.

Conclusion

The use of an equation of state for calculating thermophysical properties requires adequate parameters that are difficult to estimate when data are lacking.

In this paper, a new group contribution method that allows calculating the SAFT parameters is proposed. It is applied here on five different chemical families. The basic concept underlying the approach is that because of the physical ground of the equation, the group parameters could be easily transferable. This means that the contribution of, for instance, a CH₂ group in an alkane, in an alcohol or in an olefin should have the same contribution to the equation of state parameter values.

Group parameters have been obtained on both vapor pressure and saturated liquid volume data of several representative compounds for each treated family in a sequential procedure. The results show a good representation of the regressed data.

Moreover, we even observe that the extrapolation of this method to very heavy molecules (ex: C₃₂) results in property predictions that are of the same order as if the parameters had been fitted on the molecule data themselves. We therefore consider this method as very encouraging for prediction.

Future steps consist in extension of this approach to other chemical families, including alkyl isomers of the *n*-alkanes and extension to mixtures.

List of symbols

AAD = average absolute deviation
EOS = equation of state
GC = group contribution method
SAFT = statistical associating fluid theory
SAFT-0 = original version of the SAFT equation of state [45]
SAFT-VR = SAFT with a variable range potential [49]
DIPPR = design institute for physical property data
 a = reduced molar Helmholtz free energy (res, seg, hs, assoc, etc.)
 a_0 = segment reduced molar Helmholtz free energy (seg), per mole of segments
 d = temperature-dependant hard sphere diameter
 d_{liq} = liquid molar density ($1/v_{liq}$)
 F_{reg} = regression function
 G^E = excess molar Gibbs energy
 k = Boltzmann's constant $\approx 1.381 \times 10^{-23}$ J/K
 m = effective number of segments within the molecule (segment number)
 N_{Av} = Avogadro's number $\approx 6.023 \times 10^{23}$ molecules/mol
 N_{pt} = number of data points
 P = Pressure
 R = gas constant
 S = number of association sites on a molecule
 T = temperature, K
 T_c = critical temperature
 v = molar volume, v_{liq} = liquid molar volume
 X^A = mole fraction of molecules *not* bonded at site A

Greek letters

D^{AB} = "strength of interaction" between sites A and B
 e/k = dispersion energy of interaction between segments, K
 e^{AB}/k = association energy of interaction between sites A and B
 h = pure component reduced density
 k^{AB} = volume of interaction between sites A and B
 l = range parameter of the SAFT-VR equation of state
 s = segment diameter, \AA°

Subscripts

liq = liquid
reg = regression

Superscripts

A, B, C, D, ... = association sites
res = residual
seg = segment
hs = hard sphere
disp = dispersion
assoc = association
cal = calculated
exp = experimental

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